Surface Science 223 (1989) 551–568
North-Holland, Amsterdam

PHOTOELECTRON SPECTROSCOPIC STUDIES ON THE DISSOCIATION OF CO ON POTASSIUM-DOSED Rh(111) SURFACE

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Received 7 June 1989; accepted for publication 25 July 1989

Adsorption of CO has been investigated on clean and potassium-dosed Rh(111) surfaces by means of TDS, UPS, XPS and work function measurements. CO adsorbs molecularly at 90–300 K on Rh(111) dosed with K up to a monolayer coverage. No spectroscopic evidences were found for the dissociation of CO in the coadsorbed layer heated to near the onset temperature of CO desorption. A well detectable dissociation of CO was observed following electron bombardment of the coadsorbed layer. The effect of potassium on the reaction of adsorbed oxygen and carbon (produced by electron bombardment or by decomposition of ethylene) was also examined. Formation of chemisorbed CO at $\theta_K = 0.33$ occurred at 400–500 K, far below the desorption of CO from this surface. A promoting effect of potassium was established. It was concluded that CO desorbs from K-dosed Rh(111) without undergoing a significant dissociation, and the isotopic scrambling between labelled CO proceeds likely via a nondissociative mechanism.

1. Introduction

We recently investigated the adsorption of CO_2 on the potassium-promoted Rh(111) surface [1,2]. Potassium dramatically influenced the bonding and reactivity of CO_2 adsorbed on Rh(111); it increased the binding energy, induced the formation of new adsorption states and initiated the dissociation of CO_2. From the UPS and XPS data it was concluded that the activation of CO_2 through formation of the CO_2^- anion radical, which dissociates to CO and O at 131–179 K at low K coverage ($\theta_K \simeq 0.1$) and disproportionates into carbonate and CO above 238 K at $\theta_K = 0.3$. It remained an open question whether the CO formed in the above processes underwent further dissociation or retained its molecular identity until its desorption. Analysis of the data obtained did not reveal any indication of the dissociation of CO in the CO_2 + K/Rh system. This might be due to the presence of absorbed oxygen, as the dissociation of CO has been established before on the K-promoted Rh(111) surface [3,4].

The dissociation of CO on transition metal surfaces has been the subject of extensive research, as it is of strong relevance to the catalytic synthesis of

hydrocarbons and alcohols. The unambiguous establishment of CO dissociation is not always very simple; several potentially disturbing factors should be excluded before a final conclusion is reached. This is well demonstrated by the controversy on the dissociation of CO on clean Rh surfaces [5–13]. It now appears certain that CO adsorbs predominantly molecularly on clean Rh surfaces under UHV conditions and the probability of CO dissociation at 370–870 K is negligible [7,8]. On supported Rh and at ambient pressure the dissociation of CO has been detected only above 473 K [12,13]. The reactivity of other Pt metals is practically identical: no dissociation of CO occurs up to 300 K under UHV conditions [14].

The situation could obviously be different in the presence of potassium which drastically decreases the C–O stretching frequencies and increases the binding energy of CO for all transition metals. Although the extents of these changes are practically the same [15], the absorbed CO even on potassium-dosed Pt metals exhibited different reactivities [15–30]. On Rh(111), it was found that potassium adatoms not only weaken the C–O bond, but can ultimately lead to its rupture [3,4]. This was established from isotopic mixing experiments but was not confirmed by spectroscopic studies. The same conclusion was reached for Fe(100), Fe(111) [16], Ni(100) [17,18] and Ni(111) [19,20] surfaces, where the dissociation of CO was observed at 300–400 K. On the other hand, dissociation of CO has not been observed or reported for the K-promoted Ni(100) [21], Ru(001) [22–24], Pt(111) [25–27], Pd(100) and Pd(110) [28–30] surfaces in this temperature range.

In the present study, the interaction of CO with K-dosed Rh(111) is examined by means of TPD, $\Delta\phi$, UPS and XPS measurements, with particular attention to the dissociation of CO.

2. Experiments

The experiments were carried out in an ultrahigh-vacuum chamber with a base pressure of 5×10^{-10} Torr, equipped with a hemispherical analyzer (Leybold-Hereaus LHS-10) for UPS, XPS and AES, and a quadrupole mass spectrometer for TDS [2].

UPS were performed by using He I (21.22 eV) and He II (40.81 eV) radiation. The angles between the surface normal and the UV lamp and between the surface normal and the analyzer were 75° and 16°, respectively. Work function measurements were obtained from He I spectra. The photoelectrons were excited by Al Kα radiation (1486.7 eV) in the XPS regime. The pass energy was 50 eV and the resolution is estimated to be $\sim$ 1.2 eV. The accuracy of the determination of the position of O(1s) binding energy is $\pm$0.2 eV. The experimental data were collected with a multichannel analyzer (Tracor-Northem 1710) and a computer.

High resolution, electron-induced Auger spectra were taken in $dN(E)/dE$ mode using a lock-in amplifier (Ithaco, Dinatrac 391 A) with 0.5 eV peak-to-peak modulation, 1 μA of indicident current and 2.5 kV of incident energy. The cleaning procedure for the Rh(111) and crystal mount have been previously described [1].

Potassium was deposited on Rh(111) at room temperature by resistively heating a getter wire source (SAES getter) located 2 cm from the sample. The time required for potassium deposition was 0.5–2 min. The K coverage was calibrated using LEED, AES and TPD yield, and was described elsewhere [1,3]. A monolayer of potassium on Rh(111) corresponds to a surface density of 5.8×10^{14} atoms/cm^2 or $\theta_K = 0.36$ potassium atom per surface rhodium atom.

3. Results

3.1. Characteristics of CO + K coadsorbed layer on Rh(111)

In the first part of the experiments we confirmed the characteristics of thermal desorption of CO from clean and K-promoted Rh(111) surfaces. CO desorbs from the K-free surface in a broad peak, with $T_p = 490$ K. The total uptake of CO and the amount of CO desorbed in this peak decrease with increase of the potassium coverage. At the same time, at above $\theta_K = 0.15$ a new high temperature state develops with $T_p = 700$ K. Above $\theta_K = 0.3$, the desorption of CO mainly occurs from this high-temperature state. These features show excellent agreement with those established by Somorjai et al. [3,4].

Figs. 1a and 1b display UPS spectra from the adsorbed layer at 300 K and after gradual heating to higher temperatures. We note here that the spectra obtained following CO adsorption on clean and K-dosed Rh(111) at 100 K exhibited exactly the same features as at 300 K. As observed previously [2], the deposition of potassium on Rh(111) decreased and broadened the emission of the d-band of Rh. This effect increased with the K coverage. At $\theta_K = 0.1$, the K(3p) level appeared at 18.0 eV in the He II UPS spectrum. At monolayer coverage, the position of this peak was observed at 17.7 eV.

Adsorption of CO on K-dosed surface at $\theta_K = 0.1$ caused a shift in the K(3p) signal to lower energy, 17.8 eV (this is clearly seen in the difference spectrum). Additionally, two new signals were produced, at 8.0 and 10.9 eV. No changes in the positions and intensities of these signals were observed up to 420 K. The signals were eliminated at 540–570 K without any indication of the development of a new emission.

At near monolayer K coverage ($\theta_K = 0.33$), the coadsorbed CO enhanced the intensity of the emission of K(3p). New photoemission signals appeared at

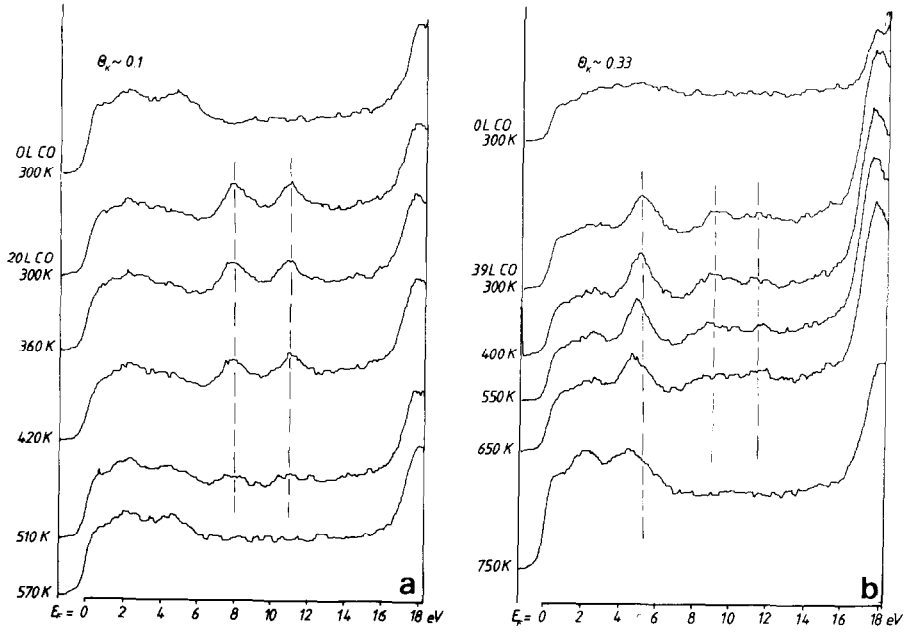


Fig. 1. HeII photoelectron spectra of adsorbed CO on K-dosed Rh(111) at different temperatures. (a) $\theta_K = 0.1$; (b) $\theta_K = 0.33$.

5.2, 9.0 and 11.5 eV. Upon heating of the adsorbed layer, the intensities of all the peaks gradually decreased above 550 K. They were eliminated between 700 and 750 K. No new emission were detected during this heat treatment. The remaining spectrum corresponds well to that of a clean Rh(111) pertubed by a small amount of potassium.

For comparison, similar studies were performed with a clean surface. The adsorption of CO in this case produced new signals at lower binding energies, 7.9 and 10.8 eV. Attenuation of these peaks occurred above 400 K; they were completely eliminated at 500 K, without producing any additional spectral features.

In another series of experiments, the coadsorbed layer of CO and K was kept at the high temperature of 604 K, just below the desorption of CO, and the UPS spectrum was registered at certain times up to 30 min. *The difference spectra taken at 300 and 600 K showed no new peaks which could be attributed to adsorbed oxygen and carbon.*

These measurements have been repeated by means of XPS. Following potassium adsorption, two signals were detected at 293.3 and 295.4 eV, which are due to spin–orbit splitting of the K(2p) level into $2p_{3/2}$ and $2p_{1/2}$ components [2].

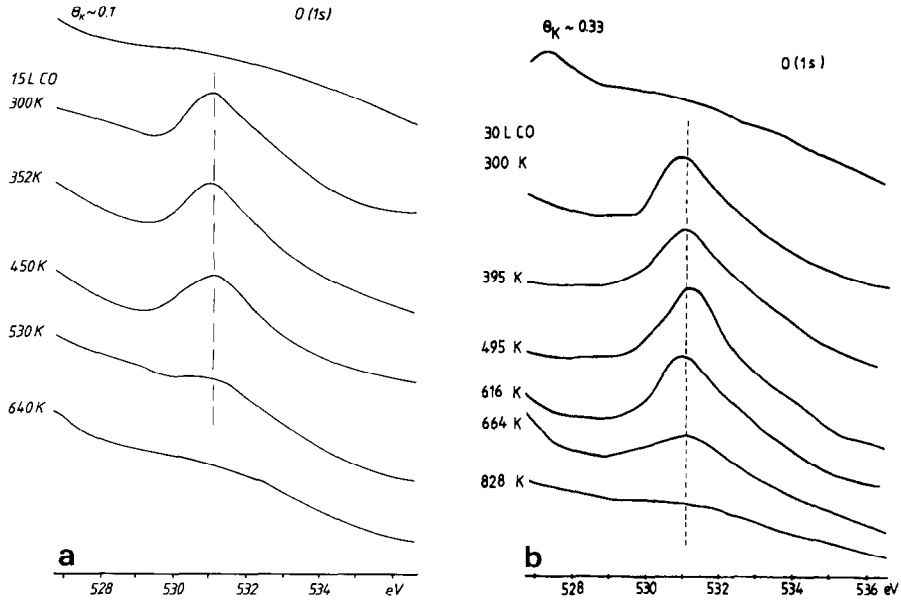


Fig. 2. X-ray photoelectron spectra of adsorbed CO on K-dosed Rh(111) at different temperatures. (a) $\theta_K = 0.1$; (b) $\theta_K = 0.33$.

The adsorption of CO on the clean Rh(111) surface produced two peaks in the XPS spectrum, at 531.4 eV for O(1s) and 285.6 eV for C(1s). In harmony with the results of UPS studies, the peaks for the clean surface decreased in intensity when the coadsorbed layer was heated above 400 K, and they vanished at about 500 K.

The adsorption of CO on potassium-dosed Rh(111) shifted the potassium signals to lower binding energy. The O(1s) and C(1s) levels appeared at same energies as for a clean surface. These peaks disappeared at 550 K for $\theta_K = 0.1$ (fig. 2a) and above 720 K for $\theta_K = 0.33$ (fig. 2b), without any significant shift to lower binding energy. When the coadsorbed layer at $\theta_K = 0.33$ was heated to 604 K near the temperature of onset of CO desorption for 10 min and then cooled back 300 K, there was no significant alteration relative to the XPS spectrum registered previously at 300 K (fig. 3). The subtraction of the clean surface sloping background gave no low energy shoulder neither for the results presented in fig. 2b nor fig. 3. The adsorption of oxygen on this surface ($\theta_K = 0.33$) produces an O(1s) peak at 530.0 eV (fig. 3).

Work function changes observed for Rh samples following the adsorption of CO and after subsequent heating can be seen in fig. 4. It may be mentioned that the work function of Rh(111) decreased linearly with K exposure up to $\theta_K = 0.17$, with $\Delta\phi = -3.5$ eV [1]. Further K deposition led to a slight increase (0.5 eV). The adsorption of CO at 300 K caused an increase in the work

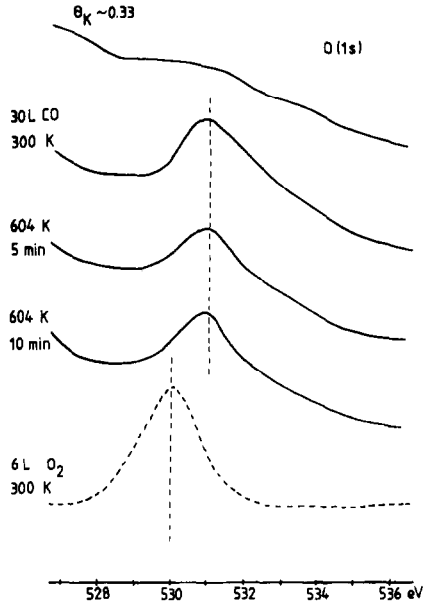


Fig. 3. Effect of annealing the adsorbed layer at 604 K on the X-ray photoelectron spectra. Adsorption temperature of CO was 300 K. The spectrum of O(1s) level after adsorption of oxygen is also shown. $\theta_K = 0.33$.

function of all samples. Upon heating of the adsorbed layer, the work function started to decrease at 350 K for the clean Rh. This decrease was sharp and continuous, and the original value was attained at 600 K. In the case of an K-promoted surface, the situation was more complex. The work function

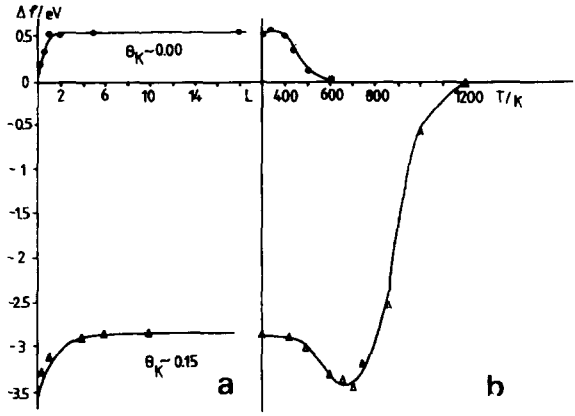


Fig. 4. Changes in the work function of clean and K-dosed Rh(111) following CO adsorption at 100 K (a) and after heating the coadsorbed layer to different temperatures (b).

decreased between 420 and 700 ($\theta_K = 0.15$–0.20), where CO desorption occurs. This was followed by a continuous increase in $\Delta\phi$ from 700 to 1200 K, which may correspond to the desorption of potassium.

3.2. Electron beam-induced reactions in the CO + K/Rh(111) system

The effects of electron beam bombardment on the thermal desorption of CO from clean and potassium-dosed surfaces are shown in fig. 5. The fraction of the crystal surface irradiated by the electron beam was about 2 mm^2. The back face was not irradiated. For the clean surface, the area of the single desorption peak was reduced by 20% and an additional broad peak appeared at around 700 K after electron bombardment (2 μA, 10 min). The area of the new peak was less than 1% of that of the main peak at this electron exposure. When the electron-bombarded surface covered by CO was heated to 600 K (above the desorption temperature of CO), traces of adsorbed oxygen and carbon were detected by AES; they disappeared completely at 800 K. The high-temperature CO desorption peak is attributed to the recombination of chemisorbed carbon and oxygen atoms, caused by impinging electrons. Electron-induced dissociation of adsorbed CO was also found on this surface in an early publication [8]. We note that according to the TPD data the electron

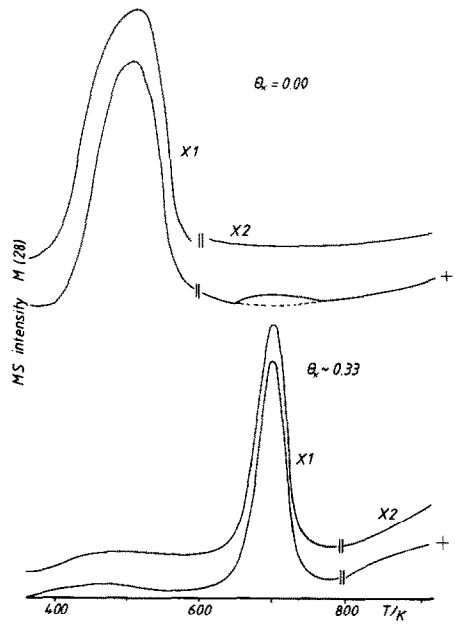


Fig. 5. Effects of electron-bombardment of adsorbed layer on the thermal desorption of CO from clean and K-dosed $\theta_K = 0.33$ Rh(111) surfaces. Curves marked with "+" are with electron bombardment.

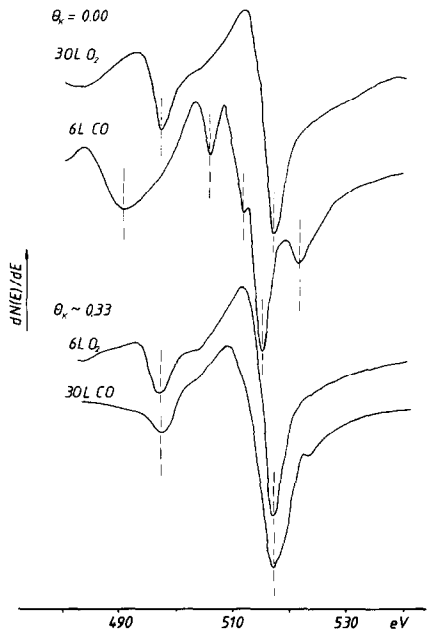


Fig. 6. Effects of electron bombardment on the electron-excited Auger fine structure of the adsorbed CO on clean and K-dosed ($\theta_K = 0.33$) Rh(111) surfaces at 300 K. Beam current was 2 μA, exposure time 10 min. AES spectra following oxygen adsorption are also shown.

beam-induced desorption of CO was more than twenty times faster than the dissociation. The same feature has been observed on Pt(111) [31].

Similar experiments were performed on the potassium-dosed surface ($\theta_K = 0.33$). Surprisingly, the electron bombardment did not cause any observable change in the position and quantity of the CO desorption (fig. 5). The beam-induced desorption was negligible in contrast with that on the clean surface.

Fig. 6 displays the electron-excited AES fine structures of O(KVV) for adsorbed CO obtained on clean and K-dosed ($\theta_K = 0.33$) surfaces at 300 K in the first derivative mode. For comparison, this figure also shows the AES fine structures of O(KLL) after oxygen adsorption on both surfaces. In these experiments, the beam exposures were the same as those used in the TDS measurements. On the clean surface, the same five-peaks structure was measured, with almost identical kinetic energies for the CO-covered surface as found in the CO/Ru(001) system using X-ray-induced AES at a polar angle of $\theta = 0°$ [32]. This structure is basically different from that of O(KLL) obtained after oxygen adsorption on Rh(111) (fig. 6), indicating that the majority of adsorbed CO preserved its molecular identity on the clean surface after electron bombardment. The situation was completely different for the K-dosed

Rh(111). In this case, the AES fine structure of O(KLL) following electron bombardment of the CO + K adlayer was practically identical with that obtained after oxygen adsorption (fig. 6). This suggests that the electron beam induced the dissociation of CO in the presence of preadsorbed potassium.

Similar conclusion can be drawn from XPS measurements at $\theta_K = 0.33$. Selected spectra are displayed in fig. 7. A significant broadening of the O(1s) signal to lower binding energy was observed when the CO-covered surface was exposed to an electron beam (2 μA, 10 min), indicating the formation of some surface oxygen.

3.3. Effects of potassium on the recombination of adsorbed O and C on Rh(111)

Potassium adatoms exerted a significant promoting influence on the recombination of adsorbed O and C produced by electron bombardment at 300 K. This is demonstrated by an experiment in which the coadsorbed layer (after electron exposure) has been heated to 450 K. The O(1s) peak shifted back to 531.2 eV, and remained constant in position and intensity even at 600 K (fig. 7). Above 750 K, there was no signal, neither for adsorbed oxygen nor for CO on this surface.

The recombination process between adsorbed oxygen and surface carbon was studied on the clean and K-dosed Rh surface in a greater detail. The carbon deposit was produced by exposing the surface to C_2H_4 at 300 K, and

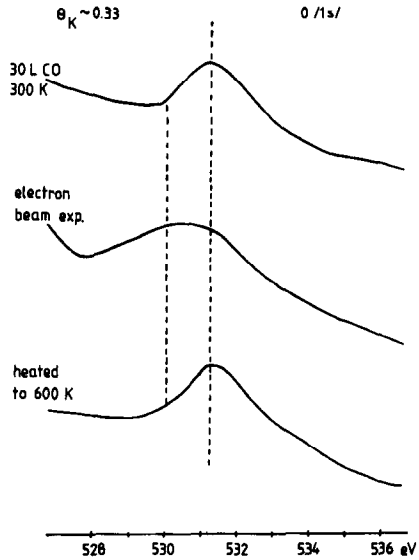


Fig. 7. X-ray photoelectron spectra of adsorbed CO on K-dosed ($\theta_K = 0.33$) Rh(111) following electron-bombardment at 300 K and subsequent heating to 600 K.

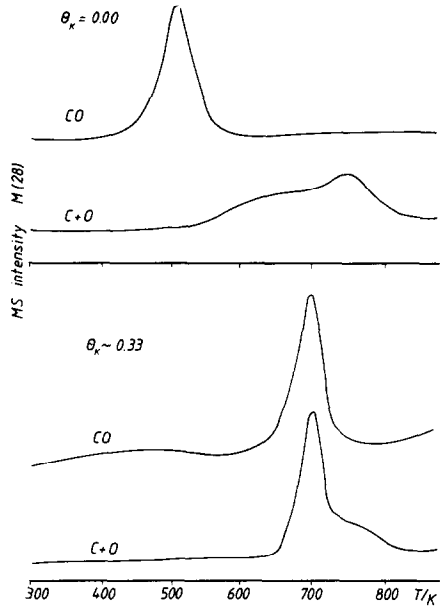


Fig. 8. Thermal desorption spectra for CO formed in the surface reaction of adsorbed C (produced by decomposition of C_2H_4) and O on clean and K-dosed Rh(111). The CO desorption curve after adsorption of CO (4×10^{14} molecules/cm^2) are also shown in both surfaces.

flashing the sample to 800 K [33]. After cooling to room temperature, the C-covered surface was exposed to oxygen. For study of the effect of potassium, the C + O-covered surface was exposed to potassium at 300 K. The relative amounts of surface carbon and oxygen were adjusted so as to obtain an oxygen to carbon ratio for an AES signal characteristic of CO adsorption. The concentration of C and O on Rh surface were the same ($(4–5)\times10^{14}$ molecules/cm^2) in all cases.

On the clean surface, the adsorbed carbon and oxygen produced CO desorption with peak maxima at 660 and 750 K (fig. 8). These desorption states appeared at higher temperatures than after CO adsorption on this surface. On the K-dosed sample, the characteristics of CO desorption due to the recombination of carbon and oxygen were the same as after CO adsorption on this surface ($T_p = 700$ K); only a shoulder appeared with $T_p = 750$ K, which can be seen on the clean surface, too (fig. 8). The amount of CO formed in the high temperature stage is about 21% of that desorbed in the peak with $T_p = 700$ K. Taking into account the characteristics of CO desorption from K-dosed Rh we conclude that the high temperature CO peak represents reaction (recombination) rate limited CO desorption. With the increase of the surface concentrations of adsorbed C and O on this surface, only the peak with $T_p = 700$ K increased further.

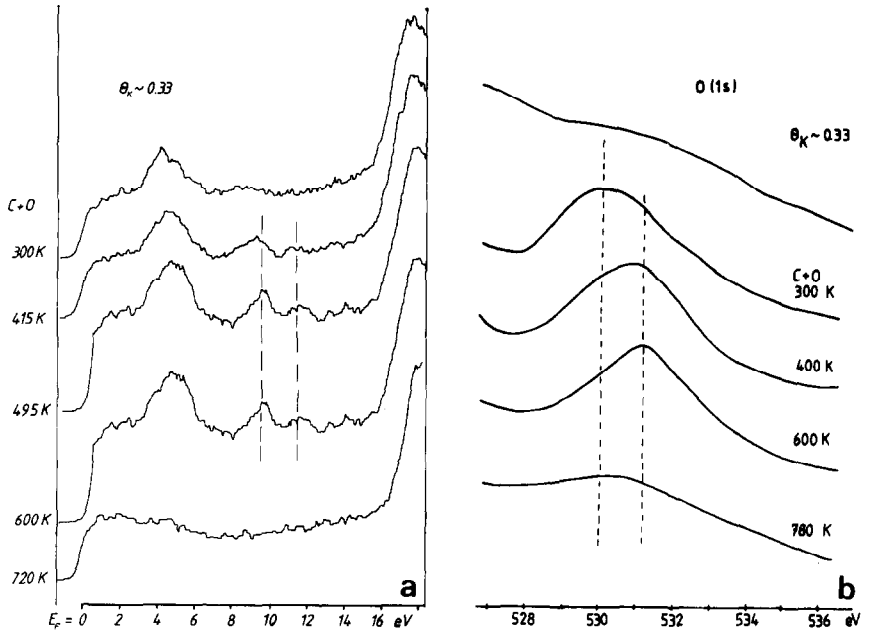


Fig. 9. Photoelectron spectra of coadsorbed C (produced by C_2H_4 decomposition) and O and K-dosed ($\theta_K = 0.33$) Rh(111) at 300 K and after heating to higher temperatures. (a) UPS; (b) XPS for O(1s) level.

Fig. 9a shows the UPS spectra of the C + O coadsorbed system at different temperatures at $\theta_K = 0.33$. Initially, the spectrum registered at 300 K exhibited broad features at 4–6 eV which correspond to the adsorbed C and O. When the surface was heated to 400 K, this feature was partially replaced by the 5.2 eV peak and two new peaks appeared at 9.4 and 11.5 eV, slightly different energies as after CO adsorption on this surface. A small increase in their intensities was observed up to 495 K. The new photoemission peaks vanished between 600 and 720 K.

Drastic changes were detected in the XPS, too (fig. 9b). The K-dosed surface on which C and O were deposited produced a peak at 530.0 eV for O(1s) at 300 K. At 400 K, the peak shifted to 531.2 eV: a small shoulder remained at 530.0 eV. At 600 K, mainly the peak at 531.2 eV was observed, indicating that the atomic oxygen reacted with carbon to produce adsorbed CO below the desorption temperature.

4. Discussion

4.1. Characteristics of adsorbed CO on K + Rh(111) surface

Although the primary aim of this work was to find spectroscopic evidence for or against the dissociation of CO on K-dosed Rh(111), we may deal briefly

with other properties of the CO + K coadsorbed layer on the Rh surface. According to previous studies [3,4], the coadsorbed layer over Rh(111) exhibits the same characteristics as other transition metals [34]: a drastic increase in the binding energy of CO, a coincident thermal desorption of CO and K at higher K coverages, a marked decrease in the CO stretching frequency, and a weakening of the C–O bond.

The present photoelectron and $\Delta\phi$ measurements provided additional evidence for the strong interaction between CO and K/Rh(111). On a clean surface, the CO adsorption at 300 K produced peaks at 7.9 eV and 10.8 eV in UPS, and 285.6 eV C(1s) and 531.4 eV O(1s) in XPS spectrum, which are in good agreement with data determined before on the Rh(100) surface [35]. The peak at 10.8 eV is assigned as emission from the 4σ level of CO and the peak at 7.9 eV is attributed to emission from unresolved 1π and 5σ states. On potassium-dosed Rh(111), the position of the 4σ level appeared at somewhat higher binding energy (10.9 eV at $\theta_K = 0.10$ and 11.2 eV at $\theta_K = 0.17$). The O(1s) level in XPS shifted to lower energy by 0.2 eV. Similar trends were observed for the CO + K/Pt(111) system, which was correlated with an enhanced back donation of electrons into the CO $2\pi^*$ orbital [27]. The work function increase found at that K coverage (fig. 4) is consistent with this picture.

A more significant shift occurred in the position of CO-induced emissions in the He II photoelectron spectrum around monolayer K coverage. In addition, a new emission was produced at 5.2 eV. It is important to point out that this peak also appeared when CO was adsorbed at 100 K on an K-dosed surface. Its intensity changed parallel with that of $1\pi/5\sigma$ and 4σ orbitals upon heat treatment. This peak was also detected after CO adsorption on Fe(110) [16a] and Ni(100) [17], and was attributed to the 2p emission of atomic oxygen formed in the CO dissociation. In these cases an intense peak developed at 5.4–6 eV when the coadsorbed layer was heated to 390–500 K, and the emissions of orbitals of CO disappeared.

The peak at 5.2 eV also occurred in the He II spectrum following adsorption of CO, CO_2 and even Ar on Ag(111) where the formation of adsorbed O was ruled out [36]. Prince and Bradshaw [36] proposed that this peak arises from umklapp-type processes, where the photoelectrons emitted off normal are scattered into the normal direction. The peak disappeared at angles of more than 25° off normal [36].

A low binding energy peak was also seen for CO adsorbed on the K/Ru(001) surface [23,37,38], where the dissociation of CO was excluded. It was interpreted by sp^2 rehybridized model having new bond (b_1, b_2) [23,37]. Another explanation was given by Heskett et al. [38], who attributed this peak to a direct interaction between the 1π orbitals of CO and potassium.

The occurrence of direct interaction at $\theta_K = 0.33$ is very likely reflected by a 0.4 eV shift of the K(3p) level to lower binding energy and by its significant

intensity increase following CO adsorption (fig. 1b). This feature was also observed for several K-dosed metals and was associated with a direct interaction between CO and potassium [38,39].

In previous works Crowell and coworkers [3,4] interpreted the effect of potassium for the CO–Rh(111) system as a long range electronic effect, i.e., by an enhanced backdonation of electrons from Rh into the 2π orbital of CO. This mechanism very likely operates at low potassium coverages, up to $\theta_K = 0.10–0.15$, where potassium exhibits mainly ionic character. This was demonstrated in our detailed study on the CO + K/Pd(100) system [30]. At high potassium coverages, where potassium exhibits mainly metallic character, there is increasing evidence for a direct chemical and/or electronic interaction between adsorbates and potassium. Formation of potassium methoxide and formate [40–42], potassium chloride [43], and potassium carbonate [1,2,44–46] were spectroscopically detected. In the case of the CO + K/M system (M = Cu(110) and Pd(110)) King and coworkers [29,47] postulated the formation of a three-dimensional oxocarbon salt "$K_2C_2O_2$" or "$K_2C_4O_4$" and concluded that the bulk of the data obtained are consistent with a salt formation model.

One piece of evidence for this model is the coincident thermal desorption traces of CO and K. On the Rh(111) surface, this coincident temperature is 700 K. However, as was pointed out in our previous work [15], the coincident peak temperature varies considerably with the nature of the metal; the difference between the highest and lowest value is 225 K. The highest value was registered for CO + K/Rh(111) which – according to the salt formation model – would mean a dramatic stabilization of potassium oxocarbon compound on Rh(111) compared to that on Cu(110), which is very unlikely. Therefore we suggest that in the direct interaction between K and CO, only $K^{\delta+}CO^{\delta-}$ surface complex is formed. As there is no, or very limited, interaction between the potassium multilayer and CO under UHV conditions, we have to assume that the above process occurs between chemisorbed CO and adjacent K on the metal surface. As a result of this interaction the binding energy of the CO is increased and, at the same time, the potassium is stabilized. Due to the mutual stabilization, the CO and K desorb in the same temperature range, characterized by an identical peak temperature. A central point of this idea is that *the bonding of CO with the host metal is preserved, and hence the stability of this surface complex is primarily determined by the strength of this bonding*. Accordingly, the variation of the coincident peak temperature with the metal simply reflects the variation in strength of CO–metal bonds which may be perturbed by potassium.

The activation of CO by the host metal is a primary requirement for the CO–K interaction. In harmony with this, no adsorption of CO was observed on either K-dosed CaF_2 [48] or Ag(111) [49,50] surfaces, where the heat of CO adsorption on K-free host compounds is less than 5 kcal/mol.

4.2. Dissociation of CO

The dissociation of CO on metal surfaces is a crucial point in the understanding the nature of CO adsorption, and this was a central issue of our work.

The isotopic mixing reaction between labelled CO,

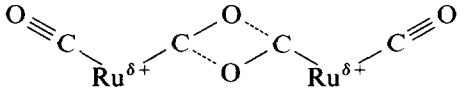
$$^{12}C^{18}O + {}^{13}C^{16}O \rightleftharpoons {}^{12}C^{16}O + {}^{13}C^{18}O,$$

which can occur as a back reaction in the CO dissociation

$$CO_a \rightleftharpoons C_a + O_a,$$

has been extensively used to establish the dissociation of CO on metal surfaces. However, some care should be exercised in evaluating the data, as there is growing evidence suggesting that CO isotopic mixing could also proceed via a nondissociative mechanism.

Bossi et al. [51] found an exchange reaction between labelled CO on Ru/Al_2O_3 but concluded that the isotopic mixing occurred in an intermolecular exchange reaction in the following surface complex



Panayotov et al. [52] also observed isotopic mixing reaction on Rh/Al_2O_3 at 373–468 K. Taking into account the other features of the interaction of CO with supported Rh, they demonstrated that isotopic mixing proceeded by a nondissociative mechanism.

This isotopic exchange reaction of CO was also noted on Cu/Al_2O_3 at 293 K [53], where a mechanism involving CO dissociation can be completely ruled out, since CO adsorbs only weakly on Cu surfaces.

A nondissociative mechanism was proposed for the exchange reaction of CO isotopes on potassium-dosed Ni(111) surface by Metiu et al. [20,54]. Although a large fraction of the CO was isotopically exchanged, the metastable quenching spectrum of the coadsorbed layer heated to 620 K (near the peak temperature of desorption) showed no evidence for the formation of adsorbed carbon and oxygen. It was suggested that the exchange reaction occurs in a coplanar four center K–CO surface complex

and does not involve a large fraction of dissociated CO.

Although EELS spectroscopy showed an anomalously weakened C–O bond on K-promoted Ru(001), TDS and EELS data provided no evidence for

irreversible CO dissociation up to 500 K [22]. Nevertheless, a complete isotopic scrambling between $^{12}C^{16}O$ was observed at $\theta_K = 0.1$, which led the authors to conclude that CO has dissociated and recombines prior to reaching the desorption temperature ($\sim$ 570 K). These features could, in principle, be explained by the above nondissociative mechanisms. However, recent work by Matsushima [55], which also included the study of the exchange reactions between ^{12}C and $^{13}C^{18}O$ and between ^{18}O and $^{12}C^{16}O$, seems to indicate that the isotopic scrambling between CO molecules on K-dosed Ru(001) is the result of dissociation and recombination processes.

Returning to the CO + KRh(111) system, Crowell et al. [4] also used the method of isotopic mixing in their study. From the analysis of their isotopic exchange data, they inferred that the dissociation was near zero until $\theta_K = 0.05$ but practically all the CO has dissociated for K coverages of $\theta_K = 0.15$. The high temperature maximum for desorption of CO and K at 700 K was attributed to the associative desorption of C and O. Note that vibrational spectroscopic data did not indicate whether CO bond cleavage occurred, since no significant M–O and M–C vibrations were detected. Nevertheless, the dissociation of CO can occur at higher temperature, as it is very likely that all vibrational measurements in ref. [4] were performed at room temperature or below.

However, the present XPS and UPS studies, extended to high temperatures, provided no evidence for the dissociation of CO even at elevated temperatures (figs. 1–3). Photoemission peaks were the same following CO adsorption at 100 and 300 K, and no new signals or shifts, indicative of CO dissociation, were produced after heating the coadsorbed layer to the desorption temperature (604 K), or holding there for 10–20 min. Accordingly, the dissociation of CO on K-dosed dosed surface at 300–604 K is very limited, if it occurs at all, and certainly much less than inferred from isotopic exchange studies, where the extent of CO dissociation was calculated to be over 80% under optimum conditions [4]. However, this result still does not rule out the possibility that the CO dissociates on K-dosed surfaces just before the CO desorption or, as was suggested by Crowell et al. [4], all the processes (i.e. dissociation, scrambling, recombination and desorption) proceed as a concerted process. To discuss this point further, we refer first to the results obtained following electron bombardment.

It was demonstrated that electron bombardment induces the dissociation of CO on both clean and K-dosed surfaces. On clean Rh, the associative desorption of CO occurred at higher temperature than the desorption of molecularly bonded CO (fig. 5). On the K-dosed surface, the extent of CO dissociation was considerably larger, which is in harmony with the previous assumption that the C–O bond is significantly weakened by potassium. The occurrence of this process was easily detected by high resolution AES, XPS and UPS measurements. The surprising result was that on K-dosed Rh(111),

the surface C and O recombined to adsorbed CO at 400–500 K, far below the desorption temperature of CO from the K-dosed sample (figs. 6 and 7). As a consequence of this, no new TPD peak was produced in the TPD spectrum.

This feature was observed in a separate study when the surface carbon was generated by the decomposition of ethylene (figs. 8 and 9). The recombination of C and O was significantly promoted by potassium adatoms; CO signals in UPS and XPS appeared even above 400 K, and CO desorbed in the same temperature range as following CO adsorption on the same K-dosed surface.

If we accept the proposal of Crowell et al. [4] for the results of isotopic exchange between $^{13}C^{16}O$ and $^{12}C^{18}O$ in the presence of K adatoms, namely that the dissociation, scrambling, recombination and desorption all occur as a concerted process, then it follows that the CO formed in the recombination of surface C and O at 400–500 K would dissociate and recombine again around 640–700 K, which is highly unlikely. *Therefore we incline to think that the isotopic scrambling for adsorbed CO on K/Rh(111) is the result of an exchange reaction in a molecular surface complex and not due to the dissociation and immidiate subsequent scrambling of surface C and O.*

5. Conclusions

(1) The major characteristics of the effect of potassium on CO adsorption on Rh(111) agree well with those observed for other Pt metals.

(2) UPS and XPS data provide no evidence for the K-induced dissociation of CO in the range of K coverage $\theta_K = 0.05–0.33$ (up to 604 K), just below the temperature of CO desorption.

(3) It appears that potassium greatly promotes the recombination of adsorbed oxygen and carbon (produced by electron bombardment or by decomposition of ethylene); the formation of chemisorbed CO at $\theta_K = 0.33$ was observed at 400–500 K.

(4) It is suggested that the isotopic scrambling between labelled CO previously observed before on K-dosed Rh(111) [4] occurs by a molecular exchange mechanism and does not involve significant dissociation of CO to carbon and oxygen.

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